Comment on "Calculated Photoemission Spectra of Na"

I call attention to serious errors in the Letter of Shung and Mahan[1] (SM), who have attempted to explain the Na photoemission data of Jensen and Plummer[2] (JP). JP observed emission peaks in the gap, near A, of Fig. 1. **k** conservation forbids such emission if Na is a (nearly) free-electron metal.

SM multiply each excited-state wave function ψ_f by a factor $\exp(-z/2\lambda)$, with $\lambda \sim 5$ Å, causing **k** conservation, $\delta(\mathbf{k})$, to be replaced by a Lorentzian convolution, $\sim[(\Delta k)^2+(\frac{1}{2}\lambda)^2]^{-1}$, over the Fermi-Dirac distribution of initial states ψ_i. This step violates mandatory requirements of time-dependent perturbation theory: ψ_f and ψ_i must be solutions of a Schrödinger equation, and ψ_f must be orthogonal to ψ_i. A 30-eV photon penetrates Na to a depth of $\sim 10^4$ Å, and so any optical excitation involves phase-coherent Bloch functions over a comparable depth. Finite-lifetime effects enter a correct theory only as an imaginary term in the electronic self-energy. Inelastic scattering of the excited electron is an incoherent process and cannot be represented by a phase-coherent (spatial) decay of ψ_f. This spatial-decay artifice (of SM) violates conservation of total momentum, necessarily obeyed by e-e scattering.

SM omit the most important term of the optical-transition matrix element (for an alkali metal and photon energy $W > 5$ eV). It has been shown[4] (for a transition made possible by the V_{110} pseudopotential) that

$$|\langle\psi_f|H'|\psi_i\rangle|^2 \sim \left|V_{110}+\frac{W^2}{W_0^2-W^2+iW\Gamma}V_L\right|^2. \quad (1)$$

The first term, $V_{110}\sim -0.25$ eV, arises from direct coupling, $\mathbf{A}\cdot\mathbf{p}$, of the electron and photon. (Incidentally, SM employed a V_{110} having the wrong sign.[3]) The second term of (1) arises from indirect coupling caused by collective oscillations of Na L shells in the photon's electric field. (Its presence is guaranteed by Newton's law and Coulomb's law and cannot be ignored.) V_L (~ 5 eV) is the L-shell contribution to V_{110}. W_0 (~ 47 eV) is the mean L-shell oscillation energy and Γ is its damping. For photon energies of interest here, this second term is 10^3 times more important than the first.

Finally, SM have no explanation for the "balcony" peaks, near B of Fig. 1. JP's emission data (for $W = 46, 48$ eV) clearly show the simultaneous presence of a free-electron peak and a balcony peak (near E_F). Indeed, the height of the balcony peak (above background) is larger than the other one. Band bending and wave-function mixing caused by a charge-density wave (CDW) explain this dramatic effect, since **k** conservation is then replaced:

$$\delta(\mathbf{k}) \rightarrow \sum_n A_n(\mathbf{k})\delta(\mathbf{k}+n(\mathbf{Q}-\mathbf{G}_{110})), \quad (2)$$

where **Q** is the CDW wave vector. Emission peaks in the gap (near A) arise from the $n=0$ term of (2), and the balcony emission arises from $n = \pm 1, \pm 2, \pm 3$.

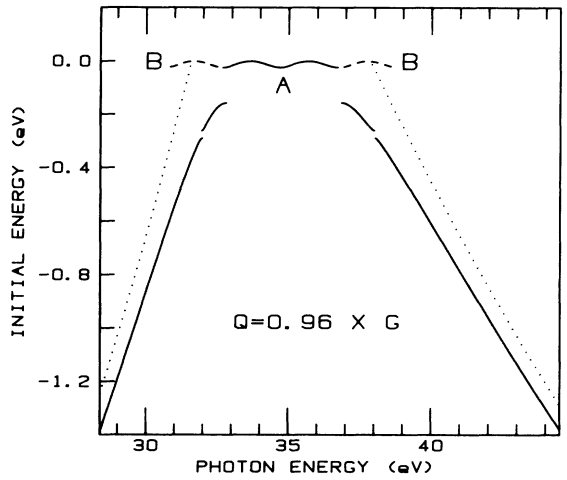

FIG. 1. Initial photoelectron energy vs photon energy for Na, from Ref. 3. The solid curve, for a CDW structure, shows emission in the gap (near A), where emission is not allowed in a (nearly) free-electron model, dotted curves. The dashed extensions at E_F (near B) are the "balcony" emission peaks allowed by the modified **k** conservation rule, Eq. (2).

At present the only explanation of JP's photoemission data involves CDW structure.[3,5] Observation of open-orbit magnetoresistance peaks, caused by the CDW in Na, has recently been reported by Coulter and Datars.[6]

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